

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08J 3/24, C08G 59/42	A1	(11) International Publication Number: WO 97/00281 (43) International Publication Date: 3 January 1997 (03.01.97)
(21) International Application Number: PCT/US96/10330 (22) International Filing Date: 13 June 1996 (13.06.96) (30) Priority Data: 08/492,179 19 June 1995 (19.06.95) US (60) Parent Application or Grant (63) Related by Continuation US 08/492,179 (CIP) Filed on 19 June 1995 (19.06.95) (71) Applicant (for all designated States except US): E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US). (72) Inventor; and (75) Inventor/Applicant (for US only): BARSOTTI, Robert, John [US/US]; 4167 Coles Mill Road, Franklinville, NJ 08322- 2260 (US). (74) Agent: COSTELLO, James, A.; E.I. du Pont de Nemours and Company, Legal/Patent Records Center, 1007 Market Street, Wilmington, DE 19898 (US).		(81) Designated States: AU, BR, CA, CN, JP, KR, MX, US, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i>
(54) Title: TWO-PACKAGE SPRAYABLE COATING COMPOSITION (57) Abstract A two-package sprayable coating composition having a binder that comprises, in one package, a chemical compound with functionality "A" and, in another package, a chemical compound with functionalities "B" and "C". Functionalities "A" and "B" react rapidly to build molecular weight without crosslinking while functionality "C" reacts with the reaction product of "A" and "B" or with "A" or with both, which reaction occurs more slowly than reaction of "A" with "B", to form a crosslinked film at cure.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgystan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

TITLE

TWO-PACKAGE SPRAYABLE COATING COMPOSITION

This invention concerns a two-package (known as a
5 2K) coating composition having a low volatile organic content
(VOC).

The exterior panels of many automobiles and other
outdoor articles are coated with a multilayer finish that contains a
colorcoat or basecoat layer and a clearcoat layer. Basecoat-
10 clearcoat systems have found wide acceptance in the past decade
as automotive finishes. Continuing effort has been directed to
such coating systems to improve the overall appearance, the clarity
of the topcoat, and the resistance to deterioration, particularly
environmental etching. Further effort has been directed to the
15 development of coating compositions having low volatile organic
content (VOC) for purposes of improved environmental safety.

A common coating composition contains epoxy resins
and polymers which include cyclic anhydrides such as maleic
anhydride and itaconic anhydride polymers and copolymers
20 reacted with epoxy functional compounds. Other efforts to improve
coating properties have suggested use of hydroxyl resins in
combination with isocyanates to form urethane coatings. U.S.
4,755,581 concerns coating compositions having epoxy and
hydroxyl functionality on separate molecules. The patent does not
25 suggest the differential cure rate necessary to maximize solids
content. Applicants effect solids maximization by use of a binder
component that is normally expected to be volatile at the cure
temperature, a very active catalyst, and epoxy and hydroxyl
functionality in the same molecule.

30 With respect to the environmental impact of using
solvent-based coatings, it is common for these to be employed in
outdoor applications, such as clear and color coating on
automobiles, storage tanks, rail cars, ships, bridges, utility
structures, and the like. Public concerns over the emission of
35 volatile organic compounds have made it desirable to coat such
articles using compositions having relatively high solids content.

SUMMARY OF THE INVENTION

This invention concerns a heat-curable, two-package sprayable coating composition with a volatile organic content of no more than about 2.5 pounds per gallon and a binder that

5 comprises:

i) an organic chemical compound having a weight average molecular weight less than about 2,000, a polydispersity not exceeding about 1.5, and functionality "A";

10 ii) an organic chemical compound having a weight average molecular weight less than about 2,000, a polydispersity not exceeding about 1.5, and functionalities "B" and "C"; and

iii) an optional catalyst to promote a differential reaction rate of "A" with "B" and "C";

wherein:

15 one of components i and ii is normally volatile at the cure temperature;

functionality "A" and "B" react very rapidly with each other upon mixing to build molecular weight without crosslinking, while retaining the volatile component;

20 functionality "C" reacts with the reaction product of "A" and "B" or with "A" or with both, which reaction occurs more slowly than the reaction of "A" with "B", to form a crosslinked film at cure; and

25 functionality "A" is separated from functionalities "B" and "C" until just prior to spraying.

Preferred functionality "A" is selected from one or more of anhydride, hydroxyl, amine, isocyanate, carboxylic acid, aziridine, carbodiimide, acrylate, methacrylate, and the like.

30 Preferred functionality "B" is selected from one or more of anhydride, hydroxyl, amine, isocyanate, carboxylic acid, aziridine, carbodiimide, acrylate, methacrylate, and the like.

By "polydispersity" is meant weight average molecular weight divided by number average molecular weight, both measured by gel permeation chromatography.

35 Preferred functionality "C" is selected from one or more of hydroxyl, isocyanate, melamine, epoxy, carboxylic acid, anhydride, ketamine, aldimine, carbonate, oxazoline, silane, and the like.

It is common to use low molecular weight volatile compounds, such as solvents, to lower the viscosity of a coating for spray application. These compounds, because of their volatility, lower the measured weight solids of the coating and thus increase VOC. This invention concerns a method of reacting these types of volatile compounds into the film to preclude evaporation, thus reducing VOC. Increasing the overall reaction rate alone would result in a coating with a very short pot life and very poor flow and leveling. This invention accomplishes this incorporation through the use of sequential reactions. Using a noncrosslinking fast reaction to incorporate volatile components and a slower crosslinking reaction to cure the film allows for a coating with excellent appearance, flow and leveling, sag resistance and film properties at very low VOC.

One skilled in the art will appreciate which of functional groups "A", "B", and "C" to react to achieve rapid noncrosslinking reactions and which to react to achieve slow cure (crosslinking). Typical representative "A" plus "B" reactions (very rapid):

anhydride + hydroxyl
anhydride + amine
isocyanate + primary amine
isocyanate + secondary amine
acid + aziridine
acid + carbodiimide
amine + pendant acrylate/methacrylate.

Typical "C" plus reaction product of "A+B" and/or "A" (slower reaction rate than above):

hydroxyl + isocyanate
hydroxyl + melamine
hydroxyl + epoxy
acid + epoxy
anhydride + epoxy
amine + epoxy
isocyanate + ketamine
isocyanate + aldimine
isocyanate + epoxy
isocyanate + acid

acid + melamine
carbonate + amine
acid + oxazoline
silane + silane
5 silane + hydroxyl.

For this combination of reactions to work well in forming a coating, the product of "A" plus "B" should be soluble or compatible in the final coating or be able to melt at the cure temperature to form a uniform coating film.

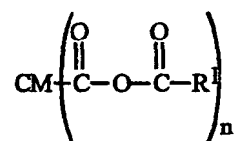
10

DETAILS OF THE INVENTION

Compound (i)

Compounds meeting the described requirements of low molecular weight, low polydispersity, and presence of "A" functionality are generally known to one skilled in the art. What has not been appreciated heretofore is the effect that can be achieved with a composition formed from the reaction product of such compound(s) with compounds (ii) described hereafter.

Typical specific compounds that meet the recited requirements include monomeric cyclic anhydrides, such as methylhexahydro phthalic anhydride, and anhydride oligomers having a central organic moiety and more than one pendant, noncyclic anhydride moiety bonded to each central moiety. The anhydride is asymmetrical, and preferably contains a moiety represented by the following formula:



wherein (CM) is a central moiety, (R¹) is an organic moiety, and n is a number of pendant anhydride groups that averages greater than one.

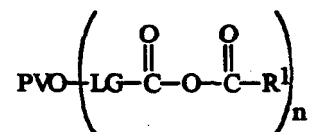
The central moiety can be aliphatic, cycloaliphatic or aromatic, with a plurality of anhydride groups bonded to it. Alternatively, it can contain a plurality of repeating units which are bonded to one or more pendant anhydride groups. Examples of suitable non-polymeric central moieties are those derived from multifunctional alcohols such as pentaerythritol,

trimethylolpropane and neopentyl glycol. The multifunctional alcohols are reacted with cyclic, monomeric anhydride such as methyl hexahydrophthalic anhydride to give a multifunctional acid-containing moiety. The resulting product is then reacted with
 5 ketene to form the pendant anhydride.

The central moiety is linked to more than one noncyclic anhydride moiety, on average. It is preferably linked to at least 2 noncyclic anhydride groups on average and more preferably to at least 3 noncyclic anhydride groups on average.
 10 The anhydride equivalent weight (formula weight per anhydride group) is preferably about 200 to 1000. The molecular weight (weight average) of the anhydride resin is preferably 400 to 1,000, and the anhydride resin preferably has 3 to 4 pendant, noncyclic anhydride moieties bonded to each central moiety.

15 Each anhydride moiety is typically terminated by an organic group (R^1). This group is preferably aliphatic and more preferably alkyl. It preferably contains no more than about 6 carbon atoms, more preferably no more than 4 carbon atoms, and is most preferably methyl.

20 The oligomeric anhydride can optionally contain a polyvalent organic moiety (PVO) that is linked to a plurality of anhydride groups by a plurality of pendant linking groups (LG), as illustrated in the following formula:



The linking group (LG) can contain, for example, ester linkages,
 25 alkylene groups, ether linkages, urethane linkages and combinations of them. The polyvalent organic group can contain, for example, a polyvalent alkyl or aromatic group. The combination of the polyvalent organic moiety (PVO) and the linking groups (LG) forms the central moiety (CM) as previously described. The central
 30 moiety can optionally contain other functional groups in addition to the pendant noncyclic anhydride groups, including pendant acid groups. The molar ratio of pendant noncyclic anhydride groups to pendant acid groups in the oligomeric anhydride is preferably at least about 25:75, more preferably about 50:50, and more highly

preferably about 75:25. Most preferably, the anhydride contains substantially no pendant acid groups. The central moiety can also contain minor quantities of cyclic anhydride moieties.

Another example of an "A" compound is an isocyanate, such as the isocyanurate trimer of hexamethylene diisocyanate which can be reacted with compounds (ii) such as volatile amine/alcohols or amine/aldimines.

Compound (ii)

Compounds meeting the described requirements of low molecular weight, low polydispersity, and presence of "B" and "C" functionalities are generally known to one skilled in the art. What has not been appreciated heretofore is the effect that can be achieved with a composition formed from the reaction product of such compound(s) with compounds (i) described above.

Typical specific compounds that meet the recited requirements include compounds that contain both epoxy and hydroxyl functionality such as: sorbitol polyglycidyl ether (DCE-358 from Dixie Chemical), mannitol polyglycidyl ether, pentaerythritol polyglycidyl ether, glycerol polyglycidyl ether, low molecular weight epoxy resins such as epoxy resins of epichlorohydrin and bisphenol-A and low molecular weight resins containing glycidyl methacrylate or glycidyl acrylate and a hydroxyl functional monomer such as hydroxy ethyl acrylate.

Other examples of compound (ii) are volatile amine/alcohols or amine/aldimines which can be reacted and retained in the film through rapid reaction with isocyanate functional crosslinkers such as the isocyanurate trimer of hexamethylene diisocyanate. Another example of compound (ii) is a volatile epoxy/hydroxyl-containing compound such as glycidol which can react with the anhydrides described with respect to component (i).

Optional Catalyst (iii)

Compositions of this invention can contain a functional amount of active catalyst to increase the reaction rate between "A" and "B" at temperatures below the bake temperature, preferably at room temperature. This accentuates the difference in rate between the volatile incorporation reaction and the

crosslinking reaction. Particularly beneficial catalysts in the anhydride/hydroxyl/epoxy reaction are tertiary amine catalysts such as triethylene diamine, bis(2-dimethyl aminoethyl)ether and N,N,N1,N1-tetramethylethylenediamine.

5

Other Ingredients:

The compositions of the present invention can contain a surface tension reducing agent in an amount sufficient to wet the surface onto which it is applied. A wide variety of surfactants can
10 be used, depending on the particular coating formulation and the surface onto which it is applied. However, conventional silicone and fluorocarbon surfactants have been found to be satisfactory.

The coating compositions of the present invention are formulated into high solids coating systems and can be dissolved
15 in at least one solvent. Preferred solvents include aromatic hydrocarbons such as petroleum naphtha or xylenes; ketones such as methyl amyl ketone, methyl isobutyl ketone, methyl ethyl ketone or acetone; esters such as butyl acetate or hexyl acetate; and glycol ether esters such as propylene glycol monomethyl ether acetate.

The coating compositions of the present invention can also contain conventional additives such as pigments, stabilizers, rheology control agents, flow agents, toughening agents and fillers. Such additional additives will, of course, depend on the intended use of the coating composition. Fillers, pigments, and other
20 additives that would adversely affect the clarity of the cured coating will not be included if the composition is intended as a clear coating.

Other optional ingredients can be added to the coating compositions to achieve a desired balance of properties, including
30 epoxy functional oligomers such as di- and polyglycidyl esters of carboxylic acids, such as Araldite CY-184® from Ciba-Geigy, or XU-71950 from Dow Chemical and cycloaliphatic epoxies, such as ERL-4221 from Union Carbide; and monomeric or polymeric alkylated melamine formaldehyde resins or silane-containing
35 oligomers or resins. Small amounts of high molecular weight acrylic or polyester resins common in the art can also be added.

The compositions of the present invention are typically applied to a substrate by conventional techniques such as

- spraying, electrostatic spraying, roller coating, dipping or brushing. A surprising aspect of this invention is the ability to spray these very low VOC coatings with excellent appearance using conventional two component equipment. The substrate is generally
- 5 prepared with a primer and/or a colorcoat or other surface preparation prior to coating with the present compositions. Clearcoats of the present coating compositions are preferably applied using conventional techniques such as application over dried waterborne basecoats.
- 10 After application to a substrate, the present compositions are cured by heating to a temperature of about 125° to 140°C for a period of about 15 to 90 minutes. The performance characteristics of the final cured coating composition are excellent, providing a combination of excellent gloss and durability to
- 15 abrasion, sunlight and acid rain.

EXAMPLE 1

<u>PART 1</u>	<u>Parts by Weight</u>
Milldride® MHHPA from Milliken (70/30 weight ratio of methyl hexahydrophthalic anhydride and hexahydrophthalic anhydride)	44.62
BYK-301 (silicone flow additive from BYK-Chemie)	0.26
bis(2 dimethylaminoethyl) ether (Niax A-99 from Union Carbide)	1.49
Tinuvin 384 (UV screener from Ciba Giegy)	0.56
Tinuvin 292 (hindered amine light stabilizer from Ciba-Geigy)	1.39
<u>PART 2</u>	
XUS-71950 (diglycidyl ester of 1,2 cyclohexane dicarboxylic acid from Dow)	38.10
DCE-358 (sorbitol ether epoxy from Dixie Chemical)	12.15
Tinuvin 384	1.43
Total	100

- This composition was sprayed using a 2-component gun over a waterborne basecoat which had received a warm air
- 20 prebake to remove water. The final coating was baked for 30

minutes at 285°F. The weight solids of this clearcoat at spray was over 96% when measured at 60 min at 110°C. The film had excellent appearance, cure, hardness, and chemical resistance.

5

EXAMPLE 2

<u>PART 1</u>	<u>Parts by Weight</u>
Milldride® MHHPA	39.47
25% tetra butyl phosphonium chloride in propylene glycol monomethylether acetate	1.71
20% BYK 301 in methylethyl ketone (silicone flow add from BYK Chemie)	1.11
25% NIAx A-99 in methylethylketone (tertiary amine from Union Carbide)	7.38
Tinuvin 384	1.76
Tinuvin 292	1.23
<u>PART 2</u>	
XUS-71950 (diglycidyl ester from Dow)	31.43
DCE-358 (sorbitol ether epoxy from Dixie Chemical)	13.27
butyl acetate	2.64
Total	100

These two parts were mixed and sprayed over a waterborne basecoat which had received a warm air prebake to remove water. The clear was sprayed at Fischer #2 cup viscosity = 45 sec. The cure was 30 min at 265°F. The clear film build was 2-2.5 mils. The spray solids of this clearcoat was 89+% by weight. The film had excellent appearance and cure (hardness and solvent) resistance (against methylethylketone).

10

EXAMPLE 3

<u>PART 1</u>	<u>Parts By Weight</u>
Milldride® MHHPA	22.4
20% BYK-301 (BYK Chemie)	0.63
25% NIAx A-99 in methylethylketone	3.0
butyl acetate	3.0

PART 2

sorbitol ether epoxy (DCE-358 from Dixie Chemical) 27.4

These components were mixed and applied over a primed steel panel and cured for 30 min at 265°F. The film gave excellent cure (hardness and solvent resistance) and chemical resistance.

5

EXAMPLE 4**PART 1**

	<u>Parts by Weight</u>
Milldride® MHHPA	16.8
linear anhydride*	7.0*
20% BYK 301 in propylene glycol monomethylether acetate	0.63
25% tetra butyl phosphonium chloride in propylene glycol monomethylether acetate	0.97
25% NIAK A-99 (tertiary amine from Union Carbide) in propylene glycol monomethylether acetate	3.00
Tinuvin 384	1.00
Tinuvin 292	0.7

PART 2

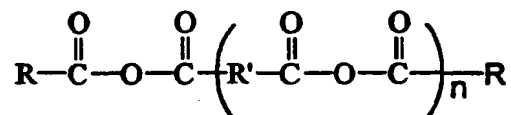
XUS-71950 (diglycidyl ester from Dow)	19.12
DCE-358 (sorbitol ether from Dixie)	6.1
butyl acetate	1.5

The components were mixed and the clear was thinned to Fischer #2 cup viscosity = 45 secs with butyl acetate and sprayed over a waterborne basecoat which had received a warm air prebake to remove water. The system was cured for 30 minutes at 265°F. The spray solids of this clearcoat was over 84% by weight. The film had excellent appearance, cure, hardness and mar resistance.

15 ***Linear Anhydride**

A crosslinking agent was prepared by mixing together 5 moles of adipic acid, 5 moles of azeleic acid, 2 moles of isononanoic acid, and 24 moles of acetic anhydride, reacting the

- monomers at 140°C while removing acetic acid as a by-product, heating the mixture to 160°C when acetic acid ceased flowing out, and removing an excess of acetic anhydride to terminate the reaction. The resulting linear anhydride was dissolved in
- 5 propylene glycol monomethyl ether acetate at a concentration of 80% by weight. The linear anhydride has the formula:



- 10 wherein R is the isononanoic group, R' is a blend of adipic and azeleic groups, and n is about 10.

EXAMPLE 5

PART 1

	Parts by Weight
Milldride® MHHPA	111.38
linear pendant anhydride*	81.6
25% tetra butyl phosphonium chloride in propylene glycol monomethylether acetate	6.78
20% BYK-301 in methylethylketone	5.69
25% NIA X A-99 in methylethylketone	20.14

PART 2

XUS-71950	119.12
DCE-358	44.3
butyl acetate	10.94

- The components were mixed and the clear was thinned
- 15 with butyl acetate to Fischer #2 cup viscosity = 60 secs. The clear was sprayed over waterborne basecoat which had received a warm air prebake to remove water. The system was cured for 30 minutes at 265°F. The spray solids of this clear was over 83% by weight. The film had excellent appearance, cure (hardness and solvent
- 20 resistance) and chemical resistance.

Linear Pendant Anhydride

The anhydride resin was prepared from a tetra-functional half-acid ester. The following constituents were charged to a reaction vessel equipped with a heating mantle, reflux condenser, thermometer, nitrogen inlet, and stirrer:

<u>Portion 1</u>	<u>Parts by Weight</u>
pentaerythritol	478.0
methyl hexahydrophthalic anhydride	2250.0
triethylamine	0.5
<u>Portion 2</u>	
xylol (135-145°C)	2250.0
Total	4978.5

Portion 1 was charged into the reaction vessel, heated to 180°C under a nitrogen blanket and held for 30 minutes. After the hold period, the reaction mixture was cooled and Portion 2 added.

The solution prepared above was used to make a linear pendant anhydride. The solution was charged into a 5L flask equipped with a stirrer and a gas inlet tube. The gas inlet tube was attached to a ketene generator and ketene was bubbled through the solution until all of the acid groups were converted to anhydride groups. Reaction progress was monitored via infrared analysis. Solvent was then removed under vacuum to give a linear pendant anhydride having 78% weight of solids and anhydride eq. wt. of 329 ±4 (on solution basis).

20

EXAMPLE 6

<u>Part 1</u>	<u>Parts by Weight</u>
Milldride® MHHPA	22.4
20% BYK-301 in propylene glycol monomethylether acetate	0.63
25% NIAX A-99 in propylene glycol monomethylether acetate	3.0
butyl acetate	4.0

Part 2

XUS-71950	19.12
DCE-358	6.1
Resimene BM-9539 (melamine resin from Monsanto)	11.2

These components were mixed and a film was applied over a primed steel panel. The film, cured for 30 minutes at 265°F, had excellent hardness and solvent resistance.

5

EXAMPLE 7

Example 2 can be modified by adding a low molecular weight acrylic resin containing glycidyl methacrylate and gamma-methacryloxypropyl trimethoxy silane to Part 2 to improve chemical resistance and marring. A typical resin which can be added at a 10% level on binder solids contains styrene/butyl methacrylate/butyl acrylate/glycidyl methacrylate/gamma-methacryloxypropyl trimethoxy silane (15/25/20/15/25 by weight %). The weight average molecular weight of this resin would be approximately 4,000.

15

WHAT IS CLAIMED IS:

1. A heat-curable, two-package sprayable coating composition with a volatile organic content of no more than about 2.5 pounds per gallon and a binder that comprises:

- 5 i) an organic chemical compound having a weight average molecular weight less than about 2,000, a polydispersity not exceeding about 1.5, and functionality "A";
- ii) an organic chemical compound having a weight average molecular weight less than about 2,000, a polydispersity
- 10 not exceeding about 1.5, and functionalities "B" and "C"; and
- iii) an optional catalyst to promote a differential reaction rate of "A" with "B" and "C";

wherein:

15 one of components i and ii is normally volatile at the cure temperature;

 functionality "A" and "B" react with each other very rapidly upon mixing to build molecular weight without crosslinking, while retaining the volatile component;

20 functionality "C" reacts with the reaction product of "A" and "B" or with "A" or with both, which reaction occurs more slowly than the reaction of "A" with "B", to form a crosslinked film at cure; and

 functionality "A" is separated from functionalities "B" and "C" until just prior to spraying.

25

2. A composition according to Claim 1 wherein functionalities "A", "B", and "C" are selected from members of the group anhydride, hydroxyl, amine, isocyanate, carboxylic acid, aziridine, carbodiimide, acrylate, methacrylate, oxazoline,

30 carbonate, melamine, epoxy, ketimine, aldimine and silane.

3. A composition according to Claim 2 wherein "A" is selected from at least one member of the group anhydride, hydroxyl, amine, isocyanate, carboxylic acid, aziridine,

35 carbodiimide, acrylate, methacrylate and silane; and the source of "B" and "C" is selected from at least one member of the group anhydride, hydroxyl, amine, isocyanate, carboxylic acid, aziridine, carbodiimide, acrylate, methacrylate, melamine, epoxy, ketimine,

aldimine, carbonate, oxazoline and silane, capable of reacting with the selected "A".

4. A composition according to Claim 3 wherein the chemical compound source of "A" is isocyanate and the chemical compound source of "B" and "C" is selected from the group hydroxyl, amine and silane.

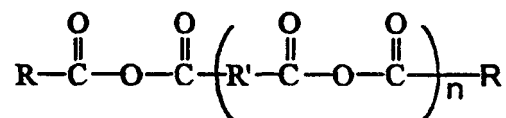
5. A composition according to Claim 3 wherein the chemical compound source of "A" is anhydride and the chemical compound source of "B" and "C" is selected from the group hydroxyl, epoxy and silane.

6. A composition according to Claim 3 wherein the chemical compound source of "A" is methyl hexahydrophthalic anhydride and the chemical compound source of "B" and "C" is a blend of a sorbitol polyglycidyl ether containing hydroxyl groups and the diglycidylester of cyclohexane dicarboxylic acid.

7. A composition according to Claim 2 wherein the polydispersity is about 1 to 1.2.

8. A composition according to Claim 3 which also contains a linear pendant anhydride having a weight average molecular weight less than about 2000, the anhydride containing central moieties and, on average, at least three pendant, noncyclic anhydride moieties bonded to each central moiety.

9. A composition according to Claim 3 which also contains a linear anhydride with two noncyclic anhydride groups and represented by the following formula:



wherein R is a monovalent hydrocarbon group having 1 to 50 carbon atoms, R' is independently selected from a bivalent

hydrocarbon group having 2 to 50 carbon atoms, the hydrocarbon groups R and R' optionally containing an ether linkage, urethane linkage or ester linkage, and n is an integer of 1 to 500.

- 5 10. A method for the spray application of a coating composition according to Claim 1 comprising contacting compound (i) with compound (ii) just prior to spraying, and spraying the combination of compounds (i) and (ii) to build molecular weight and cure the coating, optionally in the presence of a catalyst.

10

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/10330

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08J3/24 C08G59/42

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08J C08G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 257 512 (PPG INDUSTRIES, INC.) 2 March 1988	1-3,5-7, 10
Y	see page 3, line 19-57 see page 6, example A see claims 13,15,19-24 ---	1-3,5-10
Y	US,A,5 418 297 (O. ISOZAKI) 23 May 1995 see claims 1,3 see column 8, line 50-60 see column 9, line 13-22 see column 10, line 35-53 see examples 13,14 --- -/-	1-3,5-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

2 October 1996

Date of mailing of the international search report

17. 10. 96

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+ 31-70) 340-3016

Authorized officer

Hallemeesch, A

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US 96/10330

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO,A,96 01864 (E.I. DU PONT DE NEMOURS AND COMPANY) 25 January 1996 see claims 1,2 see page 2, line 10 - page 4, line 28 see page 7, line 1-13 see examples 1,2,5 ---	1-5,7-10
A	US,A,5 214 104 (C. WAMPRECHT ET AL.) 25 May 1993 see claim 1 see column 6, line 35-44 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 96/10330

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-257512	02-03-88	US-A- 4732790	22-03-88
		US-A- 4755582	05-07-88
		AU-B- 582308	16-03-89
		AU-A- 7732187	17-03-88
		CA-A- 1335341	25-04-95
		DE-D- 3787693	11-11-93
		DE-T- 3787693	28-04-94
		ES-T- 2059331	16-11-94
		JP-B- 6021275	23-03-94
		JP-A- 63084673	15-04-88
US-A-5418297	23-05-95	AU-B- 660511	29-06-95
		AU-A- 2956192	28-06-93
		BR-A- 9205464	21-06-94
		CA-A- 2091265	27-05-93
		EP-A- 0598131	25-05-94
		WO-A- 9311188	10-06-93
		NZ-A- 247076	22-12-94
WO-A-9601864	25-01-96	NONE	
US-A-5214104	25-05-93	DE-A- 4027742	05-03-92
		CA-A- 2050114	02-03-92
		EP-A- 0476323	25-03-92
		JP-A- 4234424	24-08-92

Form PCT/ISA/210 (patent family annex) (July 1992)

